REVENUE STAMPS OR REVENUE FRANKING MACHINE IMPRESSION

OFFICIAL DATE STAMP

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

APPLICATION FOR A PATENT

AND ACKNOWLEDGEMENT OF RECEIPT
(Section 30 (1) — Regulation 22)

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

	OFFICIAL APPLICATION No.	S & F REFERENCE
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FULL NAME(S) OF APPLICANT(S)

71 | GULF RESEARCH & DEVELOPMENT COMPANY

ADDRESS(ES) OF APPLICANT(S)

PITTSBURGH, Pennsylvania, U.S.A.

TITLE OF INVENTION

54 | CONVERSION OF SYNTHESIS GAS TO DIESEL FUEL IN CONTROLLED PARTICLE SIZE FLUID SYSTEM

PRIORITY IS CLAIMED AS SET OUT ON THE ACCOMPANYING FORM P.2.

THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.

21 01

THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.

21 01

THIS APPLICATION IS ACCOMPANIED BY:

- ☒ 1. ~~A single copy or a single copy in duplicate~~ or two copies of a complete specification of ....27.................. pages.
- ☒ 2. Drawings of ......1.......... sheets
- ☒ 3. Publication particulars and abstract (Form P.8. in duplicate)
- ☒ 4. A copy of Figure .... of the drawings (if any) for the abstract
- ☒ 5. Assignment of invention
- ☒ 6. Certified priority document(s) (State number)   (ONE)
- ☐ 7. Translation of the priority document(s)
- ☐ 8. An assignment of priority rights
- ☐ 9. A copy of the Form P.2. and the specification of S.A. Patent Application No | 21 | 01 |
- ☒ 10. A declaration and power of attorney on Form P.3.
- ☐ 11. Request for ante-dating on Form P.4.
- ☐ 12. Request for classification on Form P.9.
- ☐ 13.

D. M. KISCH INC. GLENCAIRN Cnr. MARKET/ECOFF STR. JHB.

| 74 | ADDRESS FOR SERVICE: | SPOOR AND FISHER, ~~...~~ |

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APPLICANTS PATENT ATTORNEYS

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COMPLETE SPECIFICATION

(Section 30(1) – Regulation 28)

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FULL NAME(S) OF APPLICANT(S)

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TITLE OF INVENTION

54	CONVERSION OF SYNTHESIS GAS TO DIESEL FUEL IN CONTROLLED PARTICLE SIZE FLUID SYSTEM

FIELD OF THE INVENTION

The present invention relates to a process for the conversion of synthesis gas to hydrocarbons in the diesel fuel boiling range. More particularly, this invention relates to the conversion of synthesis gas to straight chain paraffins in the diesel fuel boiling range using a supported cobalt catalyst having a controlled particle size dispersed in a fluid medium.

Background Information

The growing importance of alternative energy sources has brought a renewed interest in the Fischer-Tropsch synthesis as one of the more attractive direct and environmentally acceptable paths to high quality transportation fuels. The Fischer-Tropsch synthesis involves the production of hydrocarbons by the catalyzed reaction of CO and hydrogen. Commercial plants have operated in Germany, South Africa and other parts of the world based on the use of particular catalysts. The German commercial operation, for example, concentrated on the use of a precipitated

cobalt-thoria-kieselguhr fixed-bed catalyst, and a later modification where MgO, for economy reasons, replaced part of the thoria.

Attempts have been made to improve the activity of such catalyst for conversion of synthesis gas to hydro-carbons and to reduce the yield of lower boiling hydro-carbons, such as methane, so as to increase the yield of desired boiling range material.

Such attempts have included the incorporation of various promoter metals and metal oxides into the catalyst composition resulting in a wide range of catalysts and catalyst modifications in attempts to provide flexibility towards obtaining the desired boiling range product.

SUMMARY OF THE INVENTION

It has now been found in accordance with the present invention, that synthesis gas consisting essentially of CO and hydrogen can be selectively converted to a product high in straight chain paraffins in the diesel fuel boiling range (C_9-C_{21}) by contacting the synthesis gas under conversion conditions with a finely divided catalyst consisting essentially of supported cobalt and ruthenium having a controlled particle size range dispersed in a fluid medium. Surprisingly, it has been discovered that both catalyst activity and selectivity for methane are particle size dependent, such that if synthesis gas is contacted with a finely divided, supported cobalt and ruthenium catalyst having an average particle diameter of below about 110 microns, e.g., from about 10 to about 110 microns and dispersed in a fluid medium, the rate of synthesis gas conversion to hydrocarbon products is significantly increased with a corresponding reduction in the yield of methane. Moreover the rate of synthesis gas conversion to hydrocarbon product using a supported cobalt and ruthenium catalyst can be significantly increased in accordance with the process of the

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present invention over that obtainable using the same catalyst, but having a larger average particle diameter, while disposed in a fixed bed reaction zone.

According to one embodiment of the invention, it was discovered that if the supported cobalt and ruthenium catalyst of the present invention is prepared using an impregnation solution consisting essentially of a non-aqueous, organic solvent for depositing the cobalt and ruthenium and any promoter metals onto the support, the resulting catalyst can achieve a greater activity for synthesis gas conversion than is achieved by the same catalyst prepared using the conventional precipitation from aqueous solution method for depositing the metals on the catalyst support.

According to another embodiment of the present invention, it was discovered that the amount of methane produced can be less than 16 weight percent by contacting synthesis gas under conversion conditions with a finely divided catalyst consisting essentially of supported cobalt and from 0 to about 1 weight percent of a promoter selected from the group consisting of rhodium, platinum, palladium, iridium, osmium, silver and gold if the catalyst has an average particle diameter of from about 10 to about 110 microns and is dispersed in a fluid medium.

According to a still further embodiment of the present invention, a highly active catalyst can be provided for conversion of synthesis gas to straight chain paraffins in the diesel fuel boiling range by contacting synthesis gas under conversion conditions with a finely divided catalyst consisting essentially of cobalt and ruthenium supported on silica, wherein the catalyst has an average particle diameter of from about 10 to about 110 microns and is dispersed in a fluid medium, wherein the catalyst contains from about 0.05 to about 0.5 weight percent ruthenium based upon the total catalyst weight.

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According to another embodiment of the present invention, it has been found that catalyst activity for synthesis gas conversion can be increased even further by preparing the catalyst using an activation procedure in which the impregnated catalyst is subjected to the steps of (i) reduction, (ii) oxidation, and (iii) reduction herein termed "ROR activation". Surprisingly, it was found that the use of such ROR activation produces a catalyst that can achieve an even greater activity for synthesis gas conversion.

Thus, it has been found that both the rate at which synthesis gas is converted to hydrocarbons and the methane selectivity of the catalyst are catalyst particle size dependent. As will be hereinafter demonstrated, it was discovered that the CO conversion rate using the small particle size support cobalt and/or ruthenium catalyst of the present invention increased by as much as about 65 percent over that achieved using a standard commercial fixed bed catalyst while producing only one-third to one-half of the methane. Methane yield drops with decreasing particle size of the catalyst.

While fixed bed reactors have been generally preferred from an economic standpoint, such reactors have a practical lower limit in particle size. Thus, if the average particle diameter of a catalyst used in a fixed bed reactor is reduced below about 1/16th of an inch (1.6 millimeters), excessive pressure buildup occurs resulting in reactor shutdown.

In accordance with applicants' process, finely divided catalyst particles having an average particle diameter of from about 10 to about 110 microns are finely dispersed in a fluid medium, which not only enables use of small particle sized catalysts without excessive pressure buildup, but also serves as a heat transfer medium to effectively remove the exothermic heat of reaction so as to

prevent temperature runaways. Accordingly, the fluid suspension medium is "dual-functional" in that it serves to maintain the minute particles in suspension, and, also serves as a "heat transfer medium" so as to remove the

5 exothermic heat of reaction. The finely divided, supported cobalt and/or ruthenium catalyst particles of the present invention may be utilized in a fluid medium, which is either gaseous, in which case the particles are used in a fluidized bed, or liquid, in which case the particles are

10 used in a slurry.

BRIEF DESCRIPTION OF THE DRAWING

The single Figure is a schematic illustration of a preferred system for the conversion of synthesis gas to diesel fuel boiling range hydrocarbons in accordance with

15 the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the Figure, a charge stock is introduced to the system by means of line 10. The charge stock used in the process of this invention is a mixture of CO and hydrogen. Any suitable source of the CO and

20 hydrogen can be used as charge stocks and can be obtained, for example, by (i) the oxidation of coal or other forms of carbon with scrubbing or other forms of purification to yield the desired mixture of CO and H_2 or (ii) the re-

25 forming of natural gas. CO_2 is not a desirable component of the charge stocks for use in the process of this invention, but it may be present as a diluent gas.

Sulfur compounds in any form are deleterious to the life of the catalyst and should be removed. Accordingly,

30 charge stock 10 is introduced into a sulfur removal zone 12 which can utilize any conventional technique for removal of sulfur. Typical methods for the removal of sulfur, from the feed gas include amine or mono, di, or triethanolamine scrubbers, or other procedures such as the

Selexol or Stretford processes. Additionally, guard chambers containing absorbents such as ZnO can also be used.

The sulfur-free synthesis gas feed stock is then passed by means of line 14 to zone 16 where the ratio of

5 hydrogen to CO is adjusted. For example, zone 16 can comprise a shift converter in which synthesis gas and water are reacted to form an increased ratio of hydrogen to CO. Likewise, zone 16 may comprise a membrane separator for removal of hydrogen so as to adjust the hydrogen to CO

10 ratio. The molar ratio of hydrogen to CO in the charge stock can be, for example, from about 0.5:1 to about 4:1 or higher, e.g., 10:1, preferably, from about 1:1 to about 2.5:1, with 1.5:1 to about 2:1 being especially preferred.

The charge stock is then passed by means of line 18

15 to compressor 20 where the synthesis gas charge stock is compressed to the desired operating pressure. The compressed charge stock is passed by means of line 22 for admixture with recycle hydrogen and carbon monoxide introduced by line 24, and the resulting admixture is com-

20 bined in line 26 and introduced into the bottom of reactor 28.

Any suitable reactor can be utilized for the synthesis conversion process of the present invention provided that the catalyst is suspended in a fluid medium,

25 i.e., liquid or gaseous medium. Thus, suitable reactors include mechanically stirred reactors, bubble column reactors, ebullated bed reactors, or fluidized bed reactors, all of which are conventional and well known to the art. Reactors may contain blades, turbines, etc. if mechanic-

30 ally mixed. Bubble column and fluidized bed reactors may be agitated by the reactant gases. For reactors where the catalyst is suspended in a liquid medium, agitation may be accomplished by bubbling the reactant gases through the liquid medium, by addition of liquid up through the re-

35 actor, or by a combination of gas and liquid agitation.

In accordance with the present invention, an especially preferred reactor is a bubble column or ebullated bed-type reactor in which the synthesis gas charge stock is passed upwardly through finely divided catalyst particles suspended in a liquid medium as schematically presented in the Figure. Thus, reactor 28 may be provided with a distributor plate or sparger 30 in the lower portion thereof. The charge stock passes through the distributor plate or sparger and distributes the synthesis gas in the form of tiny bubbles. The synthesis gas bubbles upwardly through a suspension or slurry of the catalyst particles in the liquid medium.

As previously indicated, the catalyst particle size has a direct effect upon synthesis gas conversion rate and methane yield. Smaller particles both increase the synthesis gas conversion rate and decrease the amount of methane produced.

The catalyst particles of the present invention have an average particle diameter well below that which would be operable in a conventional fixed bed reactor, and thus, the particles must be suspended in a liquid or gaseous medium. The catalyst particles of the present invention have an average particle diameter of from about 10 microns to about 110 microns, preferably below about 80 microns, for example from about 20 or 40 microns to about 50 or 80 microns, with from about 25 to about 65 microns being especially preferred.

The catalysts of the present invention are supported cobalt and/or ruthenium-containing catalysts with from about 5 to about 25 weight percent cobalt, preferably from about 10 to about 15 weight percent cobalt based upon the total weight of the catalyst including the support.

In addition to cobalt, the catalyst may contain a Group IIIB or IVB metal oxide as a promoter. Any suitable Group IIIB or IVB metal oxide can be employed in the catalyst of the present invention, with oxides of the

actinides and lanthanides being preferred. Thus, suitable metal oxides include, for example, Sc_2O_3, Y_2O_3, Ac_2O_3, Pr_2O_3, PrO_2, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, UO_2, UO_3, U_3O_8,

5 and the like. Especially preferred metal oxides for inclusion in the catalyst of the present invention include La_2O_3, CeO_2, ZrO_2, TiO_2, HfO_2, ThO_2, and unseparated rare earth oxide mixtures high in lanthanum, praseodymium, and neodymium. Other preferred promoters include MnO_2 and

10 MgO.

Thus, the synthesis gas conversion catalyst of the .present invention can contain the Group IIIB or IVB metal oxide, in amounts of from 0 or about 0.05 to about 100 parts by weight per 100 parts by weight cobalt, preferably

15 from about 0.5 to 25 parts per 100 parts cobalt, with from about 1 to about 10 parts by weight per 100 parts by weight cobalt being especially preferred. The relatively low levels of the Group IIIB or IVB metal oxide control residual catalyst impurities. Thus, such component can be

20 omitted and the catalyst is still operative. In order to omit the Group IIIB or IVB metal oxide from the catalyst, it is merely omitted from the impregnation solution.

The cobalt and promoter metals can be supported on a suitable support, such as alumina or silica. Preferably,

25 the support is composed of gamma-alumina, eta-alumina or mixtures thereof and is present in an amount of from about 200 to about 2,000 parts by weight alumina per 100 parts by weight of cobalt, preferably between about 500 and about 900 parts of alumina per 100 parts of cobalt. Pure

30 gamma-alumina is preferred.

A preferred group of promoters includes rhodium, platinum, palladium, iridium, osmium, silver and gold on a cobalt-alumina catalyst containing from about 10 to about 15 weight percent cobalt and from about 0 to about 1

35 weight percent of such metal, preferably from about 0.01 or 0.05 to about 0.3 or 0.5 weight percent of such metal

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based upon the total catalyst weight. Based upon cobalt, the rhodium, platinum, palladium, iridium, osmium, silver or gold may be present in an amount of from about 0.01 to about 20 parts by weight, preferably from about 0.3 to

5   about 5 parts by weight per 100 parts by weight cobalt. Preferably, such catalyst is in the absence of ruthenium.

A preferred promoter for the catalyst of the present invention is a ruthenium on cobalt-alumina catalyst containing from about 10 to about 15 weight percent cobalt

10 and from about 0 to about 1 weight percent ruthenium, preferably from about 0.01 or 0.05 to about 0.3 or 0.5 weight percent ruthenium based upon the total catalyst weight. Based upon cobalt, the ruthenium may be present in an amount of from about 0.01 to about 20 parts by weight,

15 preferably from about 0.3 to about 5 parts by weight ruthenium per 100 parts by weight cobalt.

Still another preferred catalyst is a cobalt-ruthenium-Group IIIB or IVB metal oxide catalyst wherein the cobalt is present in an amount of from about 10 to

20 about 15 weight percent with from about 0.01 or 0.05 to about 0.3 or 0.5 weight percent ruthenium and from about 0 to about 5, preferably from about 0.5 to about 2 weight percent of the Group IIIB or IVB metal oxide all based upon total catalyst weight. A cobalt-ruthenium-lanthana

25 catalyst and a cobalt-ruthenium-thoria catalyst are especially preferred.

The support of the present invention is characterized as having low acidity, a high surface area and high purity. The expression "low acidity" as used in the present

30 application means that the alumina support has a Brönsted activity with H_o 1.5 which is less than 5 micromol per gram or about 10^{16} acid sites per square meter of surface area. The low acidity of the support is required in order to enable the catalyst to provide a high molecular weight

35 hydrocarbon product boiling in the diesel fuel range.

The surface area of the support of the present invention is at least 40 or 50 square meters per gram but is not so great as to become unduly microporous so as to permit reactant materials to enter the interstices of the

5   catalyst. A suitable surface area is from about 40 to about 250, preferably from about 150 to about 225 square meters per gram.

As indicated, the catalyst support of the present invention must be of high purity. The expression "high

10   purity" as used in the present application means that the catalyst when prepared on an alumina support contains negligible amounts of sulfur, silicon, phosphorus or other material having a deleterious effect on the metal dispersion or the production of high molecular weight hydrocarbon

15   products. Further, the expression "high purity" as used in the present application means that the catalyst, when prepared on silica, contains negligible amounts of sulfur, aluminum, phosphorous or other materials having a deleterious effect on the metal dispersion or the production of

20   high molecular weight products. For impurities creating acid sites, less than 5 micromol per gram should be present (about 0.01-0.1 weight percent depending on molecular weight). The deleterious effect of acidity is isomerization and cracking of intermediate olefins, removing them

25   from chain growth and producing a low molecular weight product.

The method employed to deposit the catalytic metals of the present invention onto the support involves the use of a nonaqueous, organic impregnation solution consisting

30   essentially of a soluble cobalt salt and a ruthenium salt and a soluble Group IIIB or IVB salt i.e., thorium or lanthanum salt, in order to achieve the necessary metal loading and distribution required to provide the highly selective and active catalyst of the present invention.

35

Initially, the support is treated by oxidative cal-
cination at a temperature in the range of from about 300°
to about 900°C, preferably from about 450° to about 750°C.

Meanwhile, a nonaqueous organic solvent solution of
5   the metal salts is prepared. The nonaqueous organic sol-
vent of the present invention is a non-acidic liquid which
is formed from moieties selected from the group consisting
of carbon, oxygen, hydrogen and nitrogen, and possesses a
relative volatility of at least 0.1. The expression "rela-
10   tive volatility" as used in the present application is
defined as the ratio of the vapor pressure of the solvent
.to the vapor pressure of acetone, as reference, when mea-
sured at 25°C.

Suitable solvents include, for example, ketones, such
15   as acetone, butanone (methyl ethyl ketone); the lower alco-
hols, e.g., methanol, ethanol, propanol and the like;
amides, such as dimethyl formamide; amines, such as butyla-
mine; ethers, such as diethylether; hydrocarbons, such as
pentane and hexane; tetrahydrofuran; and mixtures of the
20   foregoing solvents. Acetone is the preferred solvent.

The amount of solvent utilized is an amount that is
at least equivalent to the pore volume of the support uti-
lized, but not greater than five times the support pore
volume. For example, a commercially available gamma-
25   alumina useful in the present invention has a pore volume
of between about 0.2 to about 0.7 cubic centimeters pore
volume per gram of alumina.

Suitable cobalt salts include, for example, cobalt
nitrate, cobalt acetate, cobalt carbonyl, cobalt acetyl-
30   acetonate, or the like with cobalt nitrate and cobalt car-
bonyl [$Co_2(CO)_8$] being especially preferred. When using
cobalt carbonyl, the catalyst must be prepared in an air
and water free atmosphere to avoid oxidation of the car-
bonyl. Likewise, any suitable ruthenium salt, such as
35   ruthenium nitrate, chloride, acetate or the like may be
used. Ruthenium acetylacetonate is preferred. Similarly,

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inorganic salts or organometallic compounds of rhodium, platinum, palladium, iridium, osmium, silver or gold promoters may be used. Any suitable Group IIIB or Group IVB metal salt, such as thorium nitrate, thorium acetate, lan-
5 thanum nitrate, lanthanum acetate, or the like can be employed. In general, any metal salt or organometallic compound which is soluble in the organic solvent of the present invention and will not have a poisonous effect on the catalyst can be utilized. Thorium nitrate and lanthanum
10 nitrate are especially preferred.

Next, the calcined alumina support is impregnated in .a dehydrated state with the non-aqueous, organic solvent solution of the metal salts. Thus, the calcined alumina should not be unduly exposed to atmospheric humidity so as
15 to become rehydrated.

Any suitable impregnation technique can be employed including techniques well known to those skilled in the art so as to distend the catalytic metals in a uniform thin layer on the catalyst support. For example, the
20 cobalt and thoria can be deposited on the support material by the "incipient wetness" technique. Such technique is well known and requires that the volume of impregnating solution be predetermined so as to provide the minimum volume which will just wet the entire surface of the sup-
25 port, with no excess liquid. Alternatively, the excess solution technique can be utilized if desired. If the excess solution technique is utilized, then the excess solvent present, e.g., acetone is merely removed by evaporation. Thus, the impregnation solution can be added in
30 excess, namely, up to five times the pore volume of the support, or can be added using just enough solution to fill the pore volume of the support.

Next, the impregnation solution and support are stirred while evaporating the solvent at a temperature of
35 from about 25 to about 45°C until "dryness".

The impregnated catalyst is slowly dried at a temperature of from about 110° to about 120°C for a period of about 1 hour so as to spread the metals over the entire support. The drying step is conducted at a very slow rate in air.

If additional impregnations are needed to obtain the desired metal loading, for example, when the incipient wetness technique is used, the dried catalyst is then calcined by heating slowly in the presence of an oxygen-containing or inert, e.g. nitrogen, gas at a temperature just sufficient to decompose the metal salts and fix the .cobalt. Suitable calcination temperatures include those in the range of from about 150° to about 450°C, preferably from about 250° to about 300°C. Such impregnation, drying and calcination can be repeated until the desired metal loading is achieved. The promoter metal oxides are conveniently added together with cobalt, but they may be added in other impregnation steps, separately or in combination, either before, after, or between impregnations of cobalt.

If cobalt carbonyl is employed, contact with oxygen must be avoided. Thus, the impregnated catalyst is heated to about 200°C in an inert gas, e.g., nitrogen, or hydrogen rather than using an oxidative calcination step.

After the last impregnation sequence, the loaded catalyst support is then subjected to an activation treatment, preferably a reduction-oxidation-reduction activation treatment (ROR activation) hereinafter described.

The impregnated catalyst is preferably slowly reduced in the presence of hydrogen. The reduction is best conducted in two steps wherein the first reduction heating step is carried out at a slow heating rate of no more than from about 0.5° to about 5°C per minute, preferably from about 0.5° to about 1°C per minute up to a maximum hold temperature of 200° to about 300°C, preferably 200° to about 250°C, for a hold time of from about 6 to about 24

hours, preferably from about 16 to about 24 hours under ambient pressure conditions. In the second reduction heating step, the catalyst can be heated at from about 0.5° to about 3°C per minute, preferably from about 0.5° to about

5 1°C per minute to a maximum hold temperature of from about 250° or 300° up to about 450°C, preferably from about 350° to about 400°C for a hold time of 6 to about 65 hours, preferably from about 16 to about 24 hours. Although pure hydrogen can be employed for this reduction step, a mix-

10 ture of hydrogen and nitrogen can be utilized in order to slowly reduce the catalyst. For example, the reduction step can be conducted initially using a gaseous mixture comprising 5% hydrogen and 95% nitrogen, and thereafter, the concentration of hydrogen can be gradually increased

15 until pure hydrogen is obtained so as to slowly reduce the catalyst. Such slow reduction is particularly desirable when the metal salts utilized in the impregnation step are nitrates so as to avoid the dangers involved with an exothermic reaction in which nitrates are given off. Thus,

20 the slow reduction may involve the use of a mixture of hydrogen and nitrogen at 100°C for about one hour; increasing the temperature 0.5°C per minute until a temperature of 200°C; holding that temperature for approximately 30 minutes; and then increasing the temperature 1°C per

25 minute until a temperature of 350°C is reached and then continuing the reduction for approximately 16 hours. Reduction should be conducted slowly enough and the flow of reducing gas maintained high enough to maintain the partial pressure of water in the offgas below 1 percent, so

30 as to avoid excessive steaming of the exit end of the catalyst bed.

The reduced catalyst is passivated by flowing diluted air over the catalyst slowly enough so that a controlled exotherm passes through the catalyst bed. After passiva-

35 tion, the catalyst is heated slowly in diluted air to a

temperature of from about 300° to about 350°C in the same
manner as previously described in connection with calcina-
tion of the catalyst.

Next, the oxidized catalyst is then slowly reduced in
the presence of hydrogen in the same manner as previously
described in connection with reduction of the impregnated
catalyst.

The catalyst particles are suspended in a liquid med-
ium having sufficient viscosity to ensure that the par-
ticles remain in suspension. Additionally, the liquid
medium should have a volatility low enough to avoid loss
due to vaporization within the reactor. Additionally, the
liquid medium should be substantially free from impurities
deleterious to the reaction, such as sulfur and the like.
The liquid suspending medium may be a synthetic fluid,
such as a liquid olefin oligomer or polymer or can be a
mineral oil. Suitable synthetic hydrocarbons include
those having a viscosity of from about 4 to about 100
centistokes measured at 100°C and being sulfur, phosphorus
and chlorine-free. Likewise, a suitable mineral oil in-
cludes that having a boiling range of from about 340° to
about 850°C, preferably from about 350° to about 550°C.
An especially preferred suspending medium is higher boil-
ing liquid produced in the process of the present inven-
tion, such as hydrocarbons boiling in the range of from
about 340° to about 850°C, preferably 350° to about 550°C.

Sufficient catalyst is present in reactor 28 to pro-
vide a concentration of from about 2 to about 40 percent
by weight based upon the total slurry weight, preferably
from about 5 to about 20 weight percent, with from 7 to
about 15 weight percent being especially preferred.

The catalyst particle density should be sufficiently
low to enable suspension in the liquid phase. For exam-
ple, the catalyst support can have a density of from about

Line 19: from about 4 to about 100 centistokes = (0.0001m² /s)

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0.25 to about 0.90, preferably from about 0.3 to about 0.75 grams per milliliter, when using the metals and promoters in amounts previously described.

The synthesis feed gas is introduced into the bottom of reactor 28 by means of line 26 at a flow rate greater than the minimum fluidization velocity. In other words, the synthesis feed gas is introduced at a rate sufficient to agitate or suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to about 40, preferably from about 6 to about 10 centimeters per second. Whatever gas flow rate is selected, it should be sufficient to avoid particle settling and agglomeration.

Suitable synthesis gas conversion conditions include, for example, temperatures of from about 150° to about 300°C, preferably from about 185° to about 260°C, and most preferably from about 210° to about 230°C. The total pressure is, for example, from about 1 to about 70 atmospheres, preferably from about 6 to about 35 atmospheres, and most preferably from about 10 to about 30 atmospheres.

Light hydrocarbon products, such as a C_{20} and below fraction is withdrawn from reactor 28 by means of line 32 and passed to separation zone 34 which can comprise a series of vapor-liquid separators and a cryogenic unit for removal of hydrogen, carbon monoxide, methane and carbon dioxide from the C_{20} and below hydrocarbon fraction. The separated gasses are compressed (by a compressor not shown) and recycled by means of line 24 for further conversion, while the product diesel boiling range fraction and naphtha fractions are recovered by means of line 36. A portion of the suspending medium containing the suspended catalyst particles is withdrawn from reactor 28 by

Line 21: 1 to about 70 atmospheres = (101 to 7093kPa)
Line 22: 6 to about 35 atmospheres = (608 to 3546kPa)
Line 23: 10 to about 30 atmospheres = (1013 to 3040kPa)

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means of line 38 and passed to separation zone 40 for separation of catalysts which is withdrawn by means of line 42 from suspending liquid which is withdrawn by means of line 44 and passed to liquid separator 46. Separator 40

5   can comprise a filtration system for separating catalysts from suspending liquid, while separator 46 can comprise a distillation column for separating diesel fuel product and waxes, which are withdrawn by means of line 48 from the suspending medium which is withdrawn by means of line 50

10 from separation zone 46. A portion of the catalyst withdrawn by means of line 42 is passed by means of line 52 to a catalyst regenerator 54 while the major portion of the separated catalyst is recycled by means of lines 56 and 58 after being admixed with a portion of regenerated catalyst

15 from line 60 back to reactor 28 by means of line 62. Fresh catalyst can be added by means of lines 64 or 66 depending upon whether the fresh catalyst is in an oxidized or reduced state, respectively. If the fresh catalyst is in an oxidized state, it must be first reduced in

20 regenerator 54.

As previously indicated, the finely divided catalyst of the present invention is capable of producing CO conversion rates greater than 250 cc's of CO per gram of catalyst per hour, which is the practical limitation of a

25 commercial fixed bed reactor. Thus, the process of the present invention can provide CO conversion rates of at least 500, and preferably 700 to 1250 or higher cubic centimeters of carbon monoxide per gram of catalyst per hour, which is far in excess of that available using a commer-

30 cial fixed bed reactor.

The invention will be further described with reference to the following experimental work.

35

Example 1

A bubble column reactor was provided with catalyst particles in the form of low sulfur, alumina having a particle diameter of 20 to 105 microns (below 140 mesh) to
5 which was added 12 weight percent cobalt, 0.3 weight percent ruthenium and 0.6 weight percent of a rare earth oxide composite comprising 66.0 weight percent La_2O_3, 24.0 weight percent Nd_2O_3, 0.7 weight percent CeO_2, 8.2 weight percent PrO_2 and 1.1 weight percent other rare earth
10 oxides. The alumina had an average particle size of 52 microns. The catalyst was added to a synthetic hydrocarbon suspension liquid having a viscosity of 8 centistokes and was composed mainly of C_{40} and C_{50} isoparaffins.

15 Synthesis gas was introduced into the bottom of the bubble column through a fine mesh stainless steel screen so that the carbon monoxide and hydrogen entered the reactor in the form of small bubbles. The synthesis gas was passed through the reactor and the hydrocarbon product was
20 removed by means of heated line at the top of the reactor. Synthesis gas was continuously fed to the reactor and the temperature was initially at 225°C, but was increased and held for various periods of time while analysis of the products was made. The total pressure was maintained at
25 160 psig (10.7 atmospheres). The synthesis gas flow was maintained at 1826 standard cubic centimeters per minute, and a hydrogen to CO ratio of 1.95 to 1 was utilized.

For comparative purposes, a fixed bed reactor having a one inch I.D. with a thermowell positioned in the center
30 of the reactor was provided with 1/16 inch extrudates composed of 20.0 weight percent cobalt, 0.5 weight percent ruthenium, 1.0 weight percent of the above-described rare earth oxides and 78.5 weight percent alumina. Synthesis gas having a hydrogen to CO ratio of about 2.03:1 and a

Line 12: 8 centistokes = (8×10^{-6} m^2/s)
Line 25: 160 psig (10.7 atmospheres) = (1084kPa)
Line 29: one inch = (2.54 cm)
Line 30: 1/16 inch = (0.16 cm)

- 18 -

methane diluent (19.1 mole percent) was passed through the fixed bed reactor at a maximum stable temperature of 215°C under a feed pressure of 275 psi (18.7 atmospheres).(1895kPa) The test results are set forth in Table I below.

Table I

Test No.	1	2	3	4	5
Reactor Type:	Fixed-bed	Slurry	Slurry	Slurry	Slurry
Temperature, °C	215	225	230	235	240
CO Conversion Rate: (ccCO/gram/hour)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C_5-C_{20} (mg/gram/hour)	67	325	400	478	560
C_5+, wt. %	60.0	79.0	78.0	76.0	73.0

As seen in Table I, the CO conversion rates for the small particle sized slurry catalyst (Tests 2-5) range from about 650 to 1200 cubic centimeters per gram per hour and correspond to about 3 to 5 times the rates achieved in the fixed bed unit (Test 1) as a catalyst having a higher average particle diameter. The methane yield for the smaller catalyst was about one-half that of the fixed bed reactor containing the larger catalyst particles. Additionally, the C_5-C_{20} production rates were approximately 5 to 8 times the magnitude achieved with the larger catalyst catalyst in the fixed bed reactor.

Example 2

In order to demonstrate the effect of catalyst particle size upon conversion rate and methane production, an

experimental reactor was used which was designed for very high heat transfer and thus simulated the heat transfer characteristics of a slurry reactor.

The reactor had a 1.11 centimeter inside diameter with an 0.62 centimeter Thermowell to monitor temperature. The catalyst used in each test was prepared by impregnating cobalt nitrate, lanthanum nitrate and ruthenium acetylacetonate onto a gamma-alumina catalyst available from Akzo Chemie Nederland bv under the tradename Ketjen Grade CK-300. The alumina had a compacted bulk density of 0.67 gram per milliliter, a surface area of 190 square meters per gram and a total pore volume of 0.6 milliliter per gram. Tests were made using the aforesaid catalyst in the form of a 1/16th inch alumina extrudate impregnated with the cobalt, lanthanum and ruthenium. Smaller size particles were formed of the identical catalyst ranging from 0.16 to 0.28 millimeter average particle diameter. The 1/16th inch extrudate corresponds to a 1.6 millimeter average particle diameter.

Samples of the various size particles were tested in the amount of 10 grams each in the experimental reactor. Prior to the reactor tests, calcined samples of the catalyst were reduced in hydrogen by a series of steps including heating to 100°C, holding at 100°C for thirty minutes, increasing the temperature to 200°C over a two hour period, holding at 200°C for sixty minutes, increasing the temperature to 350°C over a one hour period and holding at 350°C overnight. After the reduction procedure, the reactor temperature was lowered to 165°C and the flow of hydrogen and carbon monoxide was begun. After one hour, the temperature was increased over a two hour period to 185°C. Tests were made under varying conditions of temperature, pressure, hydrogen to CO ratio and space velocity. Each test was run sequentially with a 24 hour onstream period. One week was required for testing each catalyst at the various conditions shown in Table II below.

Line 14:   1/16th inch = (0.16cm)
Line 18:   1/16th inch = (0.16cm)

Similarly, it is seen that at 185°C, the reaction rate increased from 147 cubic centimeters of CO per gram of catalyst per hour to 177.3 cubic centimeters of CO per gram of catalyst per hour.

5   Likewise, comparing tests 4 and 5, it is seen that the methane yield dropped from 22.7 to 10.3 weight percent methane (a decrease of 55 percent), while the yield of C_5+ correspondingly increased from 70.9 weight percent to 83.7 weight percent, which corresponds to an 18 percent in-
10   crease.

Similar results were achieved in tests 7-9 where the temperature was approximately 195°C and the hydrogen to CO ratio was reduced to 1.5. Thus, it is seen that the reaction rate increased from 195-277 cm^3/gram/hour for a cor-
15   responding reduction in particle size from 1.6 to 0.28 millimeter diameter.

The foregoing test results clearly demonstrate the significance dependence of methane selectivity and CO conversion rate upon catalyst particle size.

9. The process of claim 1 wherein said fluid medium is a liquid medium.

10. The process of claim 9 wherein said catalyst is present in said liquid medium at a concentration of from about 5 to about 20 percent by weight based upon the total slurry.

11. The process of claim 1 wherein said fluid medium is a gaseous medium.

12. The process of claim 1 wherein said catalyst comprises cobalt-ruthenium-lanthanum.

13. The process of claim 1 wherein said impregnation of the support followed an activation procedure including reduction in the presence of a reducing gas comprising hydrogen wherein the water content of the reducing gas is maintained below one volume percent.

14. The process of claim 10 wherein said liquid medium is a synthetic hydrocarbon liquid.

15. The process of claim 10 wherein said liquid medium comprises hydrocarbon conversion product.

16. The process of claim 1 wherein said impregnation is followed by an activation procedure comprising the steps, in sequence, of reduction in hydrogen, oxidation and reduction in hydrogen.

17. A process for the conversion of synthesis gas consisting essentially of CO and hydrogen to a product high in straight chain paraffins in the diesel fuel boiling range, which comprises contacting said synthesis gas under conversion conditions with a finely divided catalyst consisting essentially of supported cobalt and from 0 to about 1 weight percent of a promoter selected from the group consisting of rhodium, platinum, palladium, irridium, osmium, silver and gold, said catalyst having an average particle diameter of from about 10 to about 110 microns and being dispersed in a fluid medium, said process producing less than 16 weight percent methane.

18. The process of claim 17 wherein said catalyst has an average particle diameter of from about 10 to about 80 microns.

19. The process of claim 18 wherein said catalyst has an average particle diameter of from about 10 to about 80 microns.

20. The process of claim 17 wherein said catalyst has an average particle diameter of from about 25 to about 50 microns.

21. The process of claim 17 wherein said catalyst consists essentially of cobalt and said promoter in the absence of ruthenium.

22. The process of claim 17 wherein said cobalt is present in an amount of from about 5 to about 25 weight percent and said promoter is present in an amount of from about 0.01 to about 0.5 weight percent based upon the total catalyst weight.

23. The process of claim 17 wherein said catalyst consists essentially of cobalt on gamma alumina.

24. The process of claim 17 wherein said catalyst consists essentially of cobalt on silica.

25. A process for the conversion of synthesis gas consisting essentially of CO and hydrogen to a product high in straight chain paraffins in the diesel fuel boiling range, which comprises contacting said synthesis gas under conversion conditions with a finely divided catalyst consisting essentially of cobalt and ruthenium supported on silica, said catalyst having an average particle diameter of from about 10 to about 110 microns and containing from about 0.01 to about 0.5 weight percent ruthenium based upon total catalyst weight, said catalyst being dispersed in a fluid medium.

26. The process of claim 25 wherein said catalyst has an average particle diameter below about 80 microns.

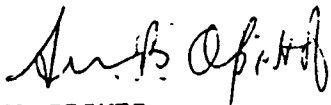27. The process of claim 25 wherein said catalyst has an

average particle diameter of from about 10 to about 80 microns.

_3.   A process according to claim 1 substantially as herein described with reference to any one of the illustrative Examples.
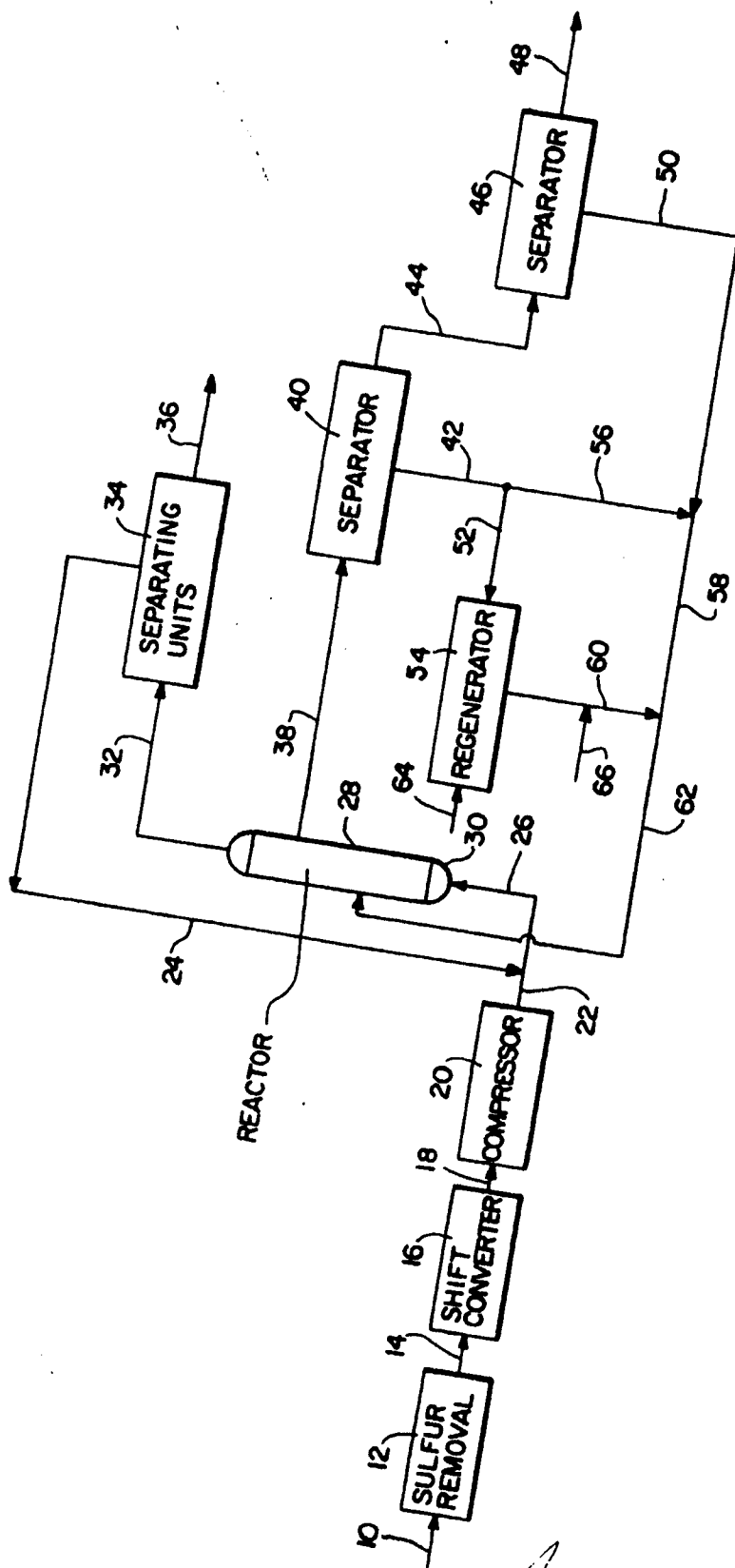
29.   A process according to claim 17 substantially as herein described with reference to any one of the illustrative Examples.

30.   A process according to claim 25 substantially as herein described with reference to any one of the illustrative Examples.

DATED THIS 15TH DAY OF JULY 1985

SPOOR AND FISHER
PATENT ATTORNEYS FOR THE APPLICANT